CURE KINETIC MODEL OF EPOXY RESINS FOR LIQUID MOLDING PROCESSES

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SUMMARY: Thermoset resins are used as constituents in fiber reinforced polymeric composites and as such the ability to characterize and describe their cure behavior is vital to numerical simulations of composite manufacturing. This study uses differential scanning calorimetry (DSC) to investigate two different diglycidyl ether of bisphenol A epoxy systems each cured with two different polyoxypropyleneamines--a diamine and triamine. The objective is to report the cure kinetic model parameters and discuss the implications of variations in cure system specification to the results. The autocatalytic cure model employed shows excellent agreement with the experimental results at the low and middle ranges of degree of conversion.

KEYWORDS: cure kinetics, process modeling, epoxy resin, DSC

INTRODUCTION

In order to optimize composite manufacturing and produce quality composites, numerical simulations have been developed to predict temperature and degree of cure during composite manufacturing. These simulations rely on the use of the energy equation, which contains a heat generation term that describes the exothermic chemical reaction of the thermoset resin. Historically, both empirical formulations that are derived from differential scanning calorimetry (DSC) and mechanistic models that are based on concentrations of reactive groups have been used to characterize the cure kinetic response. The mechanistic models are much more descriptive in a physical sense because they relate the rate of reaction to the reactive species and the stages of reaction, whereas the phenomenalogical models use algebraic manipulations and curve fitting to obtain relatively simple mathematical forms, with no consistent patterns or explanations for changes in any of the parameters. It is the empirically based, phenomenological models that have wide appeal to the composite process modeling community as the resulting expressions are ideally suited to implementation in finite difference and finite element codes.

This investigation focuses on the cure kinetic model characterization of a diglycidyl ether of bisphenol A (DGEBA) epoxy by employing the appropriate empirical form for an autocatalytic resin system [3-6]. The overall goal is to determine the cure kinetic parameters of four epoxy/curative combinations by using differential scanning calorimetry and to discuss the sensitivity of the response to variations in the model parameters.

CURE KINETIC CHARACTERIZATION

Model

The energy equation, used to describe the cure stage of composites, contains a term that is related to the heat generated from the chemical reaction. Specifically, heat generation is directly proportional to the rate of degree of cure. The degree of cure or extent of reaction,   is a measure of the crosslinks such that it ranges from zero (no crosslinks) to one (fully crosslinked). For autocatalytic epoxy-amine systems,

$$\frac{d\boldsymbol{a}}{dt} = (K_1 + K_2\boldsymbol{a})(1-\boldsymbol{a})(B-\boldsymbol{a})$$

the rate of reaction up to the point where the reaction becomes diffusion controlled is described by where B is the stochiometric ratio, i.e., the ratio of amine equivalents to the epoxide equivalents, and

$$K_i = A_i\, e^{\frac{-E_i}{RT}} \quad for\ i = 1,2$$

K_1 and K_2 are Arrhenius-type equations
where E is activation energy, A is a pre-exponential constant, R is the universal gas constant and T is temperature.

Experimental Procedure

One of the most commonly employed techniques for gathering data for cure kinetic characterization is differential scanning calorimetry (DSC). Briefly, DSC measures the heat flow into (endothermic) and out of (exothermic) a small uncured sample. Implicit in the use of this method to describe the rate of cure is the assumption that the degree of cure at any time is proportional to the cumulative heat evolved up until that time. A typical output from the DSC measurements of heat flow over time is shown in Fig. 1.

$$H = \int \frac{dQ}{dt}\, dt$$

where dQ/dt is the heat flow per unit mass. In cases where the sample undergoes complete conversion, such as in dynamic (nonisothermal) scanning through a large temperature range, the bounded area represents the maximum heat evolved for that system, and is called the heat of reaction, H_R. Based on

$$a = \frac{H}{H_R}.$$

the total heat evolved, the degree of cure a at any given time can be determined according to

$$\frac{da}{dt} = \frac{1}{H_R}\frac{dQ}{dt}.$$

Furthermore, the rate of cure during the process can be computed using
Using the data from the DSC results and equating Eqn 5 and Eqn 1, the various cure parameters can be determined for each resin system.

Materials

For this study, the epoxy resin systems consist of diglicidyl ether of bisphenol A (DER 332 and DER 383; Dow Chemical) with di-functional and tri-functional amine curatives (Jeffamine D-230 and Jeffamine T-403; Huntsman). The samples were mixed based on 1:1 stoiciometry using the amine equivalent weights and epoxy equivalent weights in Table 1. Small batches (less than 500 mg) were mixed separately for each run to reduce the effects of conversion prior to the DSC testing. Specimens were taken from the batches and ranged in sample size from 8 to12 mg.

		DER 383	181
Amine equivalent weight		Jeffamine D-230	60
		Jeffamine T-403	81

Both dynamic (nonisothermal) and isothermal scans were performed using DSC. For each resin/curative combination, a minimum of five samples were tested dynamically and two samples were tested under the same isothermal condition. In the case of the dynamic tests, each sample was exposed to the following procedure: (1) held at 323K for one minute before ramping to 483K at 10K/min, (2) cooled to 303K at 100K/min and (3) heated again at 20K/min to 483K. The last step verifies that no other reactions occurred. The isothermal scans were used to evaluate the effect of temperature on the rate and extent of reaction. Samples were held at a prescribed temperature for 120 minutes, cooled to 303K at 40K/min, held for 1 minute at 303K, then heated to 483K at 10K/min. The last step provides the means to determine the residual extent of reaction when the sample does not reach full conversion at the isothermal temperature.

ANALYSIS AND DISCUSSION

Cure Kinetic Parameters

The cure kinetic parameters obtained from the DSC testing and analysis are summarized in Table 2. Comparisons of the theoretical and experimental results over the various temperature ranges are made after the procedure for determining the cure kinetic parameters is outlined.

Table 2: Values of the cure kinetic parameters in Eqn 1 and Eqn 2

	DOW DER 332		DOW DER 383	
	Jeffamine D-230 (100:35)	Jeffamine T-403 (100:47)	Jeffamine D-230 (100:35)	Jeffamine T-403 (100:47)
H_R (J/g)	560 ± 12	489 ± 9	547 ± 13	479 ± 18
A_1 (min^{-1})	6.00×10^6	6.98×10^{10}	2.07×10^8	2.10×10^6
A_2 (min^{-1})	5.00×10^{12}	1.58×10^{10}	2.01×10^{12}	1.8×10^{12}

Fig. From the nonisothermal curve data (Fig. 1), the total heat flow was determined by using the trapezoidal rule. Normalizing these results to the sample mass yielded the heats of reaction shown in Table 2. The most pronounced distinction between the heat of reaction for different systems occurs when comparing a resin cured with a diamine to the same resin cured with a triamine. The triamine cure of each of the resins exhibits a significantly lower heat of reaction even though the ratios of resin to curative in each case were based on 1:1 stoichiometry.

The isothermal data is used to determine the cure kinetic parameters in Eqn 1 and Eqn 2. As described in the previous section, isothermal DSC was performed on two samples at four temperatures for each resin/curative combination. The temperature range selected resulted in samples that reached 30% to 95% conversion as determined by computing the cumulative heat evolved during the isothermal scan using the same trapezoidal rule method mentioned above. In order to determine the cure kinetic parameters, Eqn 1 is rewritten to obtain a linear form on the right side and to reflect the 1:1

$$\frac{d\boldsymbol{a}/dt}{(1-\boldsymbol{a})^2} = K_1 + K_2\,\boldsymbol{a}$$

stoichiometry, i.e., $B=1$.

The term on the left hand side is referred to as the reduced reaction rate. As noted by Sourour [3], the reduced reaction rate is linear when plotted with respect to the degree of cure up to the time when the reaction becomes diffusion controlled.

A typical response for the four resin systems investigated is shown in Fig. 2. When lower temperatures are being evaluated, the peak reduced reaction rate occurs at a lower degree of cure; however, the most significant difference between the plots for different temperatures is a substantial decrease in slope as the isothermal temperature is decreased. Since a different slope K_2, and y-intercept K_1, are obtained for each isothermal temperature, the best exponential fit to the K vs $1/T$ plot results in the determination of the activation energies and the pre-exponential constants as described by Eqn 2 and illustrated in Fig. 3.

Theoretical/Experimental Comparison

Fig. 4 is a typical comparison depicting the accuracy of the theoretical model to the data collected. Like the other resin systems investigated, and consistent with the findings from other researchers, the models are in excellent agreement except at low temperatures when the diffusion controlled reaction dominates. Recall that the linear portion of the reduced reaction versus degree of cure plots is limiting and the linear region decreases with decreasing temperature.

From Table 2, no trends can be observed for the cure kinetic parameters. Changes in either resin or curative have a profound effect on the cure kinetic constants; however, they mean very little to the actual response. The model constants are the result of curve fitting and while the activation energies are of the appropriate order of magnitude, the manner in which they change for the different resins or curatives is

not physically significant. Consider Fig. 5 which shows the degree of cure as a function of time for three of the four systems at 348K. The solid line represents the DER 383/D-230 system. The curve above it is the same curative but the DER 332 resin, whereas the curve below it is the same resin but the T-403 curative. So while the cure constants differ dramatically, the overall behavior is similar.

One may get the impression from the previous observation that the response is not sensitive to changes in the cure constants. Fig. 6 illustrates the high degree of sensitivity when activation energies are changed by 5% and 10%. For each resin system, the sensitivity of the pre-exponential and activation energy to the degree of cure versus time response was investigated. In all cases, the activation energies were the only parameters which exhibited a significant influence to response when they changed by as little as 5%. Since numerical simulations are the intended final purpose of these models, this sensitivity to changes in the cure constants is worth noting.

CONCLUSIONS

The four systems were modeled using an equation identified as appropriate for autocatalytic reactions. Similar to other characterizations of DGEBA resins, the model is in excellent agreement with experimental results until degrees of cure are reached where the chemical reaction becomes diffusion dominated. While the four systems have drastically different cure constants, the responses at temperatures from 313-363K were similar. This illustrates the disadvantage to these curve fitting methods in that the cure constants are not associated with physical attributes and cannot be adjusted to accommodate reasonable variations in the resin/curative combinations.

REFERENCES

1.   Prime, B. R., «Thermosets», *Thermal Characterization of Polymeric Materials*, 2nd Edition, E. A. Turi, Ed, Vol. 2, Academic Press, 1997.

2.   Yousefi, A., Lafleur, P. G., and Gauvin, R., «Kinetic Studies of Thermoset Cure Reactions: A Review», *Polymer Composites*, Vol. 18, No. 2, 1997, pp.157-168.

3.   Sourour, S. and Kamal, M. R., «Differential Scanning Calorimetry of Epoxy Cure: Isothermal Cure Kinetics», *Thermochimica Acta*, Vol. 14, 1976, pp. 40-59.

4.   Cole, K.C., «A New Approach to Modeling the Cure Kinetics of Epoxy Amine Thermosetting Resin. 1. Mathematical Development», *Macromolecules*, Vol. 24, 1991, pp. 3093-3097.

5.   Cole, K.C., «A New Approach to Modeling the Cure Kinetics of Epoxy Amine Thermosetting Resin. 1. Application to a Typical System Based on Bis[4-(diglicidylamino phenyl]methane and Bis(4-aminophenyl)Sulfone», *Macromolecules*, Vol. 24, 1991, pp. 3098-3110.

6.   Lee, W. I., Loos, A. C., and Springer, G. S., «Heat of Reaction, Degree of Cure, and Viscosity of Hercules 3501-6 Resin», *J. Composite Materials*, Vol. 16, 1982, pp. 510-520.